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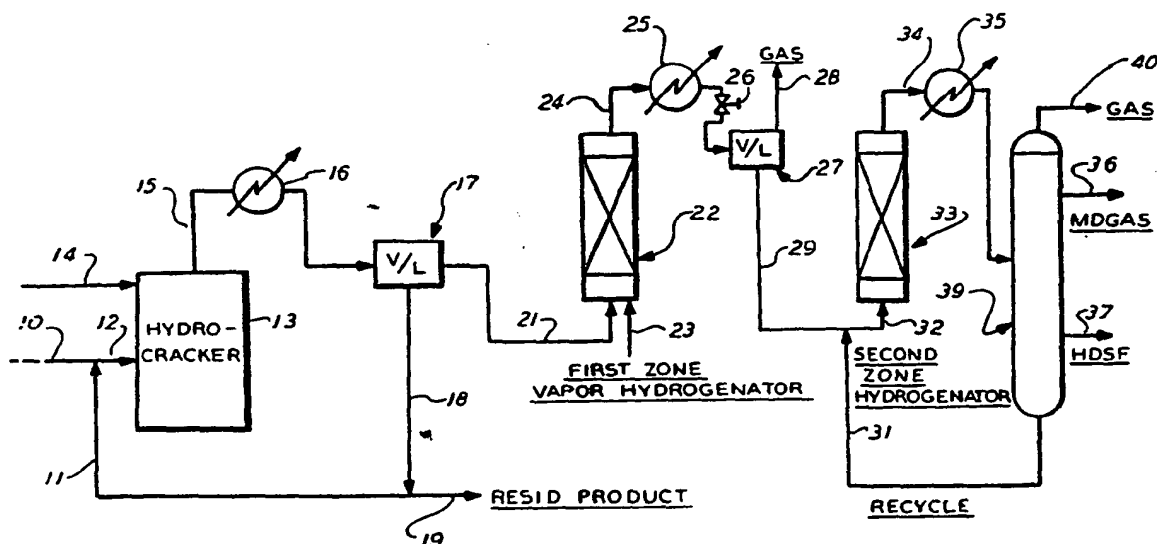
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(54) Production of high density jet fuel from coal liquids.

(57) A high density jet fuel is produced from a coal derived heavy liquid by hydrocracking to produce an effluent having a vapor fraction which includes distillates which boil below about 400 °C; followed by denitrification of the vapor fraction and hydrogenation of aromatics.

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## PRODUCTION OF HIGH DENSITY JET FUEL FROM COAL LIQUIDS

This invention relates to the production of aviation fuels, and more particularly to the production of high density jet fuels (HDJF).

Prior art processes for producing HDJF generally involve the blending of various petroleum streams that are rich in two and three ring precursors. Such a procedure presents problems in that sufficient commercial quantities of such streams may not always be available in conventional petroleum processes.

Attempts have also been made to produce HDJF by the Fisher-Tropsch method; however, in general, such attempts have not been successful.

Furthermore, attempts have been also made to produce HDJF from a fraction recovered from a synthetic crude oil produced by coal hydroliquefaction techniques.

Primary coal-derived liquids, whether derived from thermal processes or hydrogenation processes, are viscous black oils characterized by high heteroatom content and high polynuclear aromatics content. Accordingly, they are deficient in hydrogen content with respect to comparable petroleum liquids and therefore require significant hydroprocessing to upgrade them to aviation turbine fuels and other clean distillate fuel products.

A further complication with regard to their hydroprocessability is that they are typically contaminated with coke precursors (i.e., Conradson Carbon Residue, preasphaltenes, etc.) and metals derived from the coal mineral matter.

The present invention is directed to an improved process for producing high density jet fuel.

In accordance with the present invention, a high density jet fuel is produced by subjecting a coal derived heavy liquid to a series of processing steps, which includes hydrocracking to generate a vapor fraction including a distillate; denitrification of the vapor fraction; and saturation of aromatics to produce a product from which a high density jet fuel may be recovered.

The coal derived liquid is a heavy coal liquid, often referred to as a coal tar, which may be produced as a byproduct from coal gasification, coal pyrolysis, coal partial oxidation, coking, hydrolysis, hydrogenation, etc. Such a coal tar generally has at least 25% thereof boiling above 850° F and most generally at least 50% boiling above 850° F (by volume). The liquid may be derived from a variety of coals or including but not limited to lignite, bituminous and subbituminous coals, etc.

The coal derived heavy liquid is initially subjected to hydrocracking in the presence of a hydrocracking catalyst. Such hydrocracking is preferably effected in the presence of a catalyst and at conditions which maximize the yield of 524° C- distillate. In general, such hydrocracking is effected at a temperature of at least 370° C, and preferably at least 415° C. In most cases, the temperature does not exceed 468° C, and preferably does not exceed 454° C. The hydrocracking is effected at elevated pressures, with the pressure generally exceeding 1,000 psig, and most generally exceeding 2,000 psig. In most cases, the pressure is not in excess of 3,000 psig. Hydrogen is added in an amount effective to accomplish the desired hydrocracking. In most cases, the hydrocracking is operated at a hydrogen partial pressure of at least 100 atmospheres, with the hydrogen partial pressure generally not exceeding 200 atmospheres. In a preferred embodiment, the conditions are selected to provide a conversion to 524° C- distillate of at least 75%, and preferably at least 90%. In some cases, recycle of heavier materials is required in order to achieve such conversion. The hydrocracking catalyst is of a type known in the art, and generally includes a Group VI or Group VIII hydrocracking component, preferably supported on a suitable support. As representative examples of such catalyst, there may be mentioned a combination of nickel oxide and molybdenum oxide; a combination of cobalt oxide and molybdenum oxide; molybdenum oxide, etc., with the support generally being an alumina support. In most cases, the hydrocracking is accomplished at liquid hourly space velocities of from 0.1 to 3.0.

The effluent from the hydrocracking includes both a vapor and a liquid fraction. The vapor fraction is separated from such effluent, and such vapor fraction includes a distillate, with such distillate generally having a maximum nominal end point of about 400° C (atmospheric equivalent). Such vapor fraction is generally separated from the hydrocracking effluent at essentially the reaction pressures.

The vapor fraction recovered from the hydrocracking, which includes distillate, is then subjected to hydrotreating by contacting such vapor fraction with hydrogen in the presence of a hydrogenation catalyst which preferably has denitrification activity. The catalyst is preferably one which also has some hydrocracking activity to increase the content of distillates. Moreover, such catalyst should have some saturation activity to cap free radicals and to saturate olefinic unsaturation. In general, the hydrotreating is effected in a fixed bed and under conditions which reduce aromatics as well as the nitrogen content of the effluent to

acceptable levels; for example, less than 500 parts per million, and preferably less than 1 part per million. Such hydrotreating may be accomplished at temperatures of at least 315°C and preferably at least 345°C. In most cases the temperature does not exceed 400°C, and preferably does not exceed 370°C. Such hydrotreating is generally accomplished at a hydrogen partial pressure of at least 70 atm, and in most cases, the hydrogen partial pressure does not exceed 200 atm. As representative examples of suitable catalysts, there may be mentioned catalysts from groups VI and/or VIII. The catalyst is preferably supported on a suitable support. Thus, for example, the catalyst may be comprised of nickel oxide and tungsten oxide; molybdenum oxide and nickel oxide, which is preferably supported on an alumina support. In the hydrotreating, there is also a reduction in the aromatic content, i.e., saturation of aromatics.

The effluent from the hydrotreating is separated into a C<sub>5</sub>- gas stream and a C<sub>5</sub> distillate stream, with the C<sub>5</sub> distillate stream then being subjected to additional hydrogenation in the presence of a hydrogenation catalyst to saturate aromatics. More particularly, aromatics are saturated in order to generate two and three ring cycloparaffins. The hydrogenation to effect saturation of aromatics is generally accomplished at a temperature of at least 260°C and preferably at least 287°C. In most cases, the temperature does not exceed 345°C, and preferably does not exceed 320°C. In general, the saturation is accomplished at a pressure of at least 68 atm, and preferably at least 100 atm. In most cases, the pressure does not exceed about 170 atm. The saturation is generally accomplished at a hydrogen partial pressure of at least 55 atm, and generally the hydrogen partial pressure does not exceed 140 atm. Space velocities are generally in the order of 0.5 to 4.0 hours<sup>-1</sup>. The hydrogenation is preferably effected in the presence of the catalyst at conditions to provide an effluent having less than 25%, by weight of aromatics.

The catalyst which is employed for saturation of aromatics includes a hydrogenation component such as nickel oxide on silica-alumina, in acidic form, or may be comprised of molybdenum oxide and nickel oxide on alumina having high loading of molybdenum oxide at low density or may be a Y-type zeolite. It is to be understood that if there is a sufficient reduction of aromatic content during the initial hydrotreating, then within the scope of the invention the subsequent hydrogenation could be eliminated.

The effluent from the saturation is quenched, depressurized and the product is fractionated to recover a high density jet fuel fraction. In addition, there is recovered a gasoline fraction and a bottoms cut, which may be recycled to the saturation stage. The recycle cut point of the distillation bottoms can be varied between 176°C and 400°C as necessary to control the smoke point, energy density, aromatic content and freeze point of the high density jet fuel (HDJF).

In general, a high density jet fuel has at least 95 volume percent thereof boiling below about 690°F and preferably below 550°F; an API gravity of no greater than 35°, and a hydrogen content of at least 12% and preferably at least 13.5%, by weight. The 5 volume percent boiling point is preferably no less than 250°F and most preferably no less than 300°F.

The present invention will be further described with respect to an embodiment thereof which is illustrated in the accompanying drawing wherein:

The drawing is a simplified schematic flow diagram of an embodiment of a process in accordance with the present invention.

Referring now to the drawing, a coal derived heavy liquid in line 10 is combined with recycle in line 11, and the combined feed introduced into a hydrocracking zone, schematically generally indicated as 13, along with hydrogen gas in line 14.

The hydrocracking zone 13 is preferably comprised of one or more expanded bed reactors wherein the combined feed and hydrogen flow upwardly through an expanded bed of hydrocracking catalyst of the type hereinabove described. Although an expanded bed hydrocracking operation is preferred, it is possible to accomplish such hydrocracking by other processing techniques, such as a fixed bed operation employing a plurality of beds.

The hydrocracking zone is operated at conditions hereinabove described to produce an effluent containing a liquid fraction and a vapor fraction with the vapor including a distillate which boils below about 400°C.

An effluent is drawn from the hydrocracking zone 13 through line 15, and is cooled in cooler 16, with the cooled effluent being introduced into a vapor liquid separation zone, schematically generally indicated as 17. A separated liquid fraction is recovered through line 18, and all or a portion thereof is recycled through line 11, with the remaining product being recovered through line 19. The liquid fraction recovered in line 18 generally has a boiling point in excess of 400°C, and is recycled through line 11 in an amount to achieve the desired conversion in hydrocracking zone 13. The remaining 400°C plus fraction recovered through line 19 may be employed as a feed to a partial oxidation unit to produce synthesis gas.

The separated vapor fraction is recovered through line 21, and immediately introduced without condensation into a hydrotreating zone, schematically generally indicated as 22 along with hydrogen gas in

line 23. As particularly shown, the hydrotreating zone is comprised of an upflow fixed catalyst bed reactor; however, other types of reactors may be employed. The denitrification zone 22 is operated at a temperature lower than hydrocracking zone 13.

The hydrotreating zone 22 employs a catalyst, and is operated at conditions as hereinabove described in order to saturate some aromatics as well as reduce the nitrogen content of the vapor fraction. In addition, as hereinabove described, some hydrocracking may be effected in zone 22, as well as capping of free radicals and reduction of olefinic unsaturation. As shown, the denitrification is effected in the vapor phase.

A hydrotreated effluent is withdrawn from the hydrotreating zone 22 through line 24, and such effluent is quenched in cooler 25 and depressured through valve 26 into a vapor-liquid separation zone, schematically generally indicated as 27. In the vapor-liquid separation zone 27, a  $C_5^-$  gas stream is recovered through line 28 and a  $C_5^+$  liquid stream is recovered through line 29.

The liquid distillate in line 29 is combined with a recycle stream in line 31, as hereinafter described, and the combined stream in line 32 is introduced into a hydrogenation zone, schematically generally indicated as 33 which is operated with a catalyst and at conditions to effect saturation of aromatics. As particularly shown, hydrogenation zone 33 is an upflow fixed bed reactor wherein hydrogenation is effected in the liquid phase; however, it is to be understood that other types of reactors may be employed. In general, hydrogenation zone 33 is operated at a temperature lower than the temperature of hydrotreating zone 22; e.g.,  $25^\circ\text{C}$  to  $55^\circ\text{C}$  less than zone 22.

An effluent having a reduced quantity of aromatics is withdrawn from zone 33 through line 34, cooled in cooler 35, and depressurized prior to introduction into a separation and recovery zone, which is generally shown as a distillation tower 39.

As particularly shown, in distillation zone 39, there is recovered a gas fraction through line 40, a gasoline fraction through line 36, a high density jet fuel through line 37, and a recycle fraction through line 31. The recycle fraction in line 31 generally has a cut point of at least  $176^\circ\text{C}$ , and preferably at least  $204^\circ\text{C}$  with the maximum cut point being about  $400^\circ\text{C}$ . The cut point of such recycle fraction can be varied as necessary to control the smoke point, energy density, aromatics content and freeze point of the high density jet fuel product recovery through line 37.

### EXAMPLE

#### I. FEEDSTOCK

North Dakota Lignite tar oil having the following properties:

|                        |       |
|------------------------|-------|
| Specific Gravity       | 1.076 |
| Viscosity at 210F, cst | 42    |
| Pour Pt, C             | 38    |
| Elementals, wt %       |       |
| C                      | 81.99 |
| H                      | 8.53  |
| N                      | 1.10  |
| S                      | 0.72  |
| O                      | 7.42  |
| Ash                    | 0.24  |
| Distillation, °F       |       |
| IBP <sup>a</sup>       | 425   |
| 50% distilled          | 900   |

The above tar oil was subjected to expanded-bed hydrocracking over a  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalyst at 2500 psig,  $415^\circ\text{C}$ ,  $\text{LHSV} = 0.5 \text{ hr}^{-1}$ , 9800 scf/bbl  $\text{H}_2$  recycle rate.

In Case 1 (comparative)

The hydrocracked products were recovered by conventional means to produce a light oil, heavy oil and residual oil product. The heavy oil was fed to a trickle-bed hydrotreater operated at 350C, 2500 psig total pressure, 2000 psig hydrogen partial pressure, LHSV of  $1.0 \text{ hr}^{-1}$  over NiWS/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. Hydrogen consumption was 1450 scf/bbl. Nitrogen level in the product was 1 ppm. Aromatics were reduced from 80% to 35%.

The second stage product was further hydrotreated over NiO/SiO<sub>2</sub> catalyst at 310C, 2000 psig total pressure, 1800 psig hydrogen partial pressure LHSV =  $1.5 \text{ hr}^{-1}$  to produce a HDJF product containing 20% aromatics, 29 API, HHV = 130,000 Btu/gal. The yield of HDJF was 82 liq vol % on the coal tar feed.

In Case 2 (instant invention)

The hydrocracked products from the expanded-bed hydrocracker were separated in a V/L separator with the resultant vapors, without condensation, fed in an upflow manner directly to a fixed-bed hydrotreater. The latter was operated at 350C, 2000 psig total pressure, 1600 psig hydrogen partial pressure, and GHSV of  $0.75 \text{ hr}^{-1}$  over NiWS/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. Hydrogen consumption was 1150 scf/bbl. Nitrogen level in the product was 1 ppm. Aromatics were 48%.

The second stage product was further hydrotreated over NiO<sub>2</sub>/SiO<sub>3</sub> catalyst at 287C, total pressure of 1500 psig, 1200 psig hydrogen partial pressure, and LHSV of 3.0 hr. to produce a HDJF product containing 10% aromatics, 90% cycloparaffins, 26 API, HHV = 135,000 Btu/gal. The yield of HDJF was 97 liq vol % on the coal tar feed.

Thus, by directly treating the vapor fraction from the initial hydrocracking, there is obtained an improved produced in improved yields.

The present invention is advantageous in that it is possible to effectively produce HDJF from coal derived liquids. The present invention has particular applicability to liquids, derived from coal gasification and/or coal pyrolysis in that such liquids are particularly difficult to convert to HDJF in that they are more deficient in hydrogen than coal liquids derived by hydroliquefaction techniques. By proceeding in accordance with the present invention it is impossible to meet desirable specifications for HDJF; e.g., API gravity of no greater than 35°, hydrogen content of at least 12% and preferably at least 13.5%, all by weight; paraffin content of less than 10%, and an aromatic content of less than 25%. In addition, such HDJF may be produced in increased yields.

These and other advantages should be apparent to those skilled in the art from the teachings herein.

Numerous modifications and variations of the present invention are possible in light of the above teaching, and, therefore, within the scope of the appended claims, the invention may be practiced otherwise than as particularly described.

**Claims**

1. In a process for producing a high density jet fuel from a coal derived heavy liquid by cracking, denitrification and saturation of aromatics, the improvement comprising:

(a) contacting a coal derived heavy liquid with gaseous hydrogen and a hydrocracking catalyst to produce an effluent containing a liquid fraction and a vapor fraction, the vapor fraction including a distillate which boils below about 400° C; and

(b) contacting the vapor fraction with gaseous hydrogen and a hydrogenation catalyst to effect hydrogenation and denitrification thereof.

2. The process of claim 1 and further comprising (c) contacting liquid effluent derived from step (b) with gaseous hydrogen in the presence of a hydrogenation catalyst to saturate aromatics.

3. The process of claim 2 wherein the hydrogenation of step (c) reduces aromatics to less than 25% by weight.

4. The process of claim 2 wherein in step (b) the denitrified effluent has a nitrogen content of less than 500 ppm.

5. The process of claim 4 wherein hydrocracking in step (a) is effected at a conversion of at least 75% to 524° C- material.

6. The process of claim 1 wherein the coal derived heavy liquid is a coal gasification liquid.

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7. The process of claim 1 wherein the hydrocracking of step (a) is effected at a temperature of from about 370°C to 468°C.

8. The process of Claim 7 wherein the hydrogenation of step (b) is effected at a temperature of from about 315°C to 370°C.

5 9. The process of claim 8 wherein the hydrogenation of step (c) is effected at a temperature of from about 260°C to 345°C.

10. The process of claim 9 wherein the hydrogenation of step (c) is effected at a temperature lower than the hydrogenation of step (b).

10 11. The process of claim 2 wherein a high density jet fuel is recovered having at least 95 volume percent boiling below about 690°F, an API gravity of no greater than 35° and a hydrogen content of at least 12 percent by weight.

12. The process of claim 11 wherein the hydrocracking of step (a) is effected at a temperature of from about 370°C to 468°C, the hydrogenation of step (b) is effected at a temperature of from about 315°C to 370°C and the hydrogenation of step (c) is effected at a temperature of from about 260°C to 345°C.

15 13. The process of claim 11 wherein the coal derived liquid is obtained from a coal gasification process.

14. The process of claim 13 wherein the coal is lignite.

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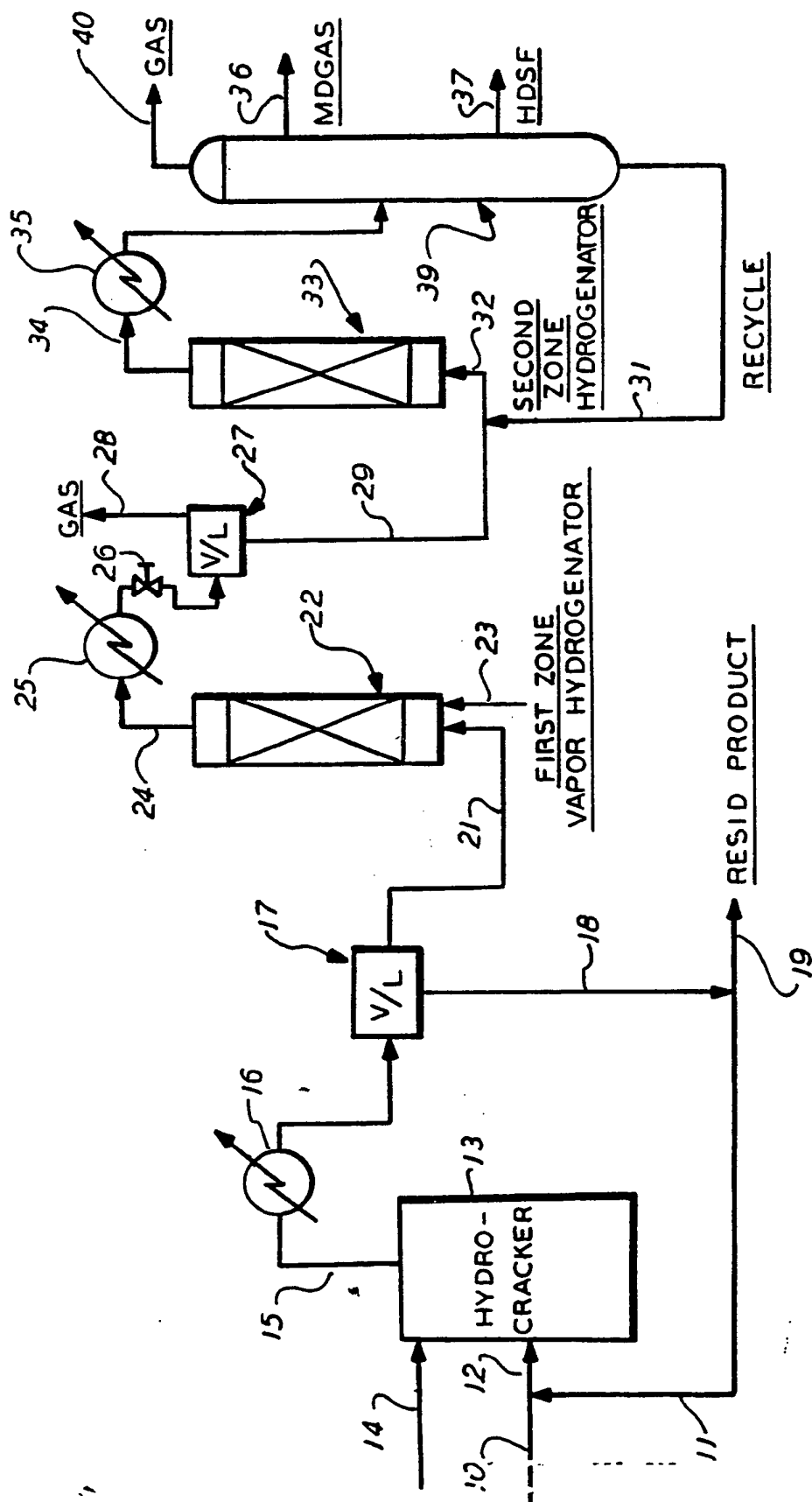
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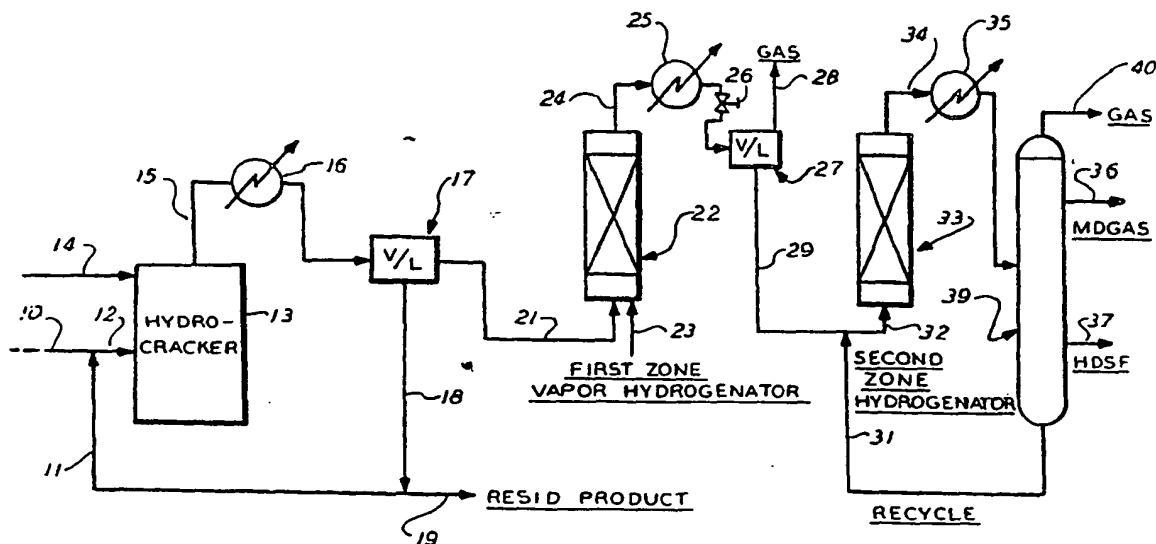
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54 Production of high density jet fuel from coal liquids.

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## EUROPEAN SEARCH REPORT

Application Number

EP 88 11 9449

| DOCUMENTS CONSIDERED TO BE RELEVANT  |  |   |  |
|--|--|---|--|
| Category   | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim   | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4) |
| A  | US-A-3 592 757 (BARAL)<br>* Claims 1,2; column 4, line 63 -<br>column 6, line 11; column 4, table;<br>column 5, table *<br>--- | 1,3,7,8<br>,9,11,<br>12   | C 10 G 1/00<br>C 10 G 65/12                    |
| A  | GB-A- 989 258 (GULF)<br>* Claims 1,2,4,5; page 2, lines<br>65-68,95 - page 3, line 127 *<br>---                                | 1,3,4,7<br>,8,9,10<br>,12   |  |
| A  | BE-A- 755 268 (TEXACO)<br>* Claims 1,2,3 *<br>---  | 1,7,8   |  |
| A  | US-A-3 143 489 (GORIN)<br>-----  |   |  |
|  |  |   | TECHNICAL FIELDS<br>SEARCHED (Int. Cl.4)       |
|  |  |   | C 10 G   |
| The present search report has been drawn up for all claims   |  |   |  |
| Place of search<br>THE HAGUE   |  | Date of completion of the search<br>08-11-1989  | Examiner<br>DE HERDT O.C.E.                    |
| CATEGORY OF CITED DOCUMENTS  |  |   |  |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another<br>document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |  | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or<br>after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>-----<br>& : member of the same patent family, corresponding<br>document |  |